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HYDRO-ISOMERIZATION OF PARAFFIN WAX*

By F. BREIMER, H. I. WATERMAN† (Hon. Fellow), and A. B. R. WEBER†

SUMMARY

Paraffin wax (average mol. wt. 375) was vaporized with hydrogen and contacted with different catalysts at 0·89–1·04 WHSV, 410°–450° C, 32–102 atm hydrogen pressure, and molar ratio $H_{2\ wax}$ 61–183. The reaction products were distilled at atmospheric pressure to 300° C and the residues subjected to a dewaxing treatment at −20° C.

Based on this separation the reaction products were regarded as *pseudo* three-component systems, the components being oil, unconverted wax, and cracked products. It was found that the oil content of the reaction products is related to the amount of cracked products and that this relationship can be expressed as an equation of the second degree containing two constants.

Based on this equation, a method for catalyst selection is suggested.

The oils obtained in the experiments have a pour point of −21° to −35° C, a viscosity index of 106–145, a viscosity at 100° F of 8·0–10·0 cS, and a viscosity at 210° F of 2·1–2·8 cS. With a platinum type catalyst a maximal oil yield of 67 per cent wt was obtained; the amount of cracked products then being 10–20 per cent wt.

INTRODUCTION

THE isomerization of petroleum waxes is a relatively new process, by means of which low pour point lubricating oils of high viscosity index and also diesel fuel of good cetane number can be produced.

The main difficulty encountered in attempts to isomerize high molecular weight paraffins is in preventing excessive cracking to lower molecular weight hydrocarbons of little value.

A fairly selective isomerization of paraffin wax has been obtained by the use of Friedel–Crafts catalysts,[1] which have been modified to decrease their cracking tendency, and by simultaneous use of a large amount of cracking suppressor (*e.g.* decahydronaphthalene). The isomerization has been carried out in the liquid phase, at atmospheric pressure, and at 20°–150° C.

The isomerization of petroleum waxes can be carried out at a faster rate and in a simpler and more selective way, with the aid of hydrogenation catalysts on acid supports, if these catalysts are used in the proper temperature range in conjunction with hydrogen under pressure. One such process comprises vaporizing the wax completely with hydrogen and contacting the wax with at least one mol of hydrogen per mol wax with supported platinum catalysts.[2]

Alkali-free activated alumina (gamma alumina) is a preferred support material. To promote the catalyst the support material is treated with hydrofluoric acid or hydrochloric acid, prior to platinization. The amount of platinum in the catalyst may vary from 0·05 to about 1 per cent by weight, while the halogen content may vary from 0·1 to 8 per cent by weight. The process is preferably carried out at a temperature between 370° and 490° C, a hydrogen pressure between 20 and 70 atm, and a contact time between 0·5 and 25 sec.

The vapour phase operation can hardly be carried out for residue waxes and other such waxes having molecular weights above about 500, since they are difficult to vaporize without thermal cracking. It has been shown that such waxes can be isomerized successfully in a liquid phase operation under about the same conditions as for the vapour phase operation, provided that contact times upwards of five minutes are employed.[3]

In order to obtain good results in the liquid phase operation it is essential that the wax is passed from the top to the bottom of the reactor, covering the catalyst surface with a thin film of liquid wax. This can be accomplished, for example, by using distribution plates in the catalyst bed. In this so-called "trickle" operation,[4] good yields of lubricating oil are obtained and the catalyst maintains its activity for a long time.

If the liquid wax is passed from the bottom to the top of the reactor, there exists no continuous hydrogen gas phase, which is believed to be necessary for keeping the catalyst surface free of carbonaceous deposits and thus maintaining its activity.

The trickle operation is not markedly superior to the vapour phase operation for the conversion of lower molecular weight waxes. An advantage of the trickle operation is the lower hydrogen recirculation and the possibility of handling residue waxes.

As platinum is rather expensive, other cheaper catalysts have recently been developed. It has been found that the isomerization of petroleum waxes can also be carried out by using oxides or sulphides of metals of group VI, left column, and group VIII of the periodic system, on acid supports.[5] Good results have, for example, been obtained by using a molybdenum–alumina-combined halogen catalyst. The operating conditions are about the same as when using platinum-containing catalysts.

In an earlier investigation,[6] two of the present

* MS received 22 May 1957.

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authors have studied the hydro-isomerization of paraffin wax, using a platinum oxysulphide–alumina-combined halogen catalyst. The degree of branching in reaction products was determined with a graphical statistical analysis based on the values of the specific refraction and specific parachor. In the present investigation more attention is given to the study of the action of different catalysts.

EXPERIMENTAL

The apparatus is similar to that described in an earlier paper.[6]

Procedure

In the experiments, the catalyst (300 ml) was charged to the reactor and the unit brought to reaction pressure with hydrogen. In order to remove air from the unit, the hydrogen was blown off and replaced by fresh hydrogen. This operation was repeated. The reactor was then heated to about 430° C and kept at this temperature for 2 hours, while hydrogen was recirculated at the desired rate. The feed-pump was then started and the reaction conditions carefully adjusted in this pre-test period, which lasted 5½ hours. After removing the pre-test period liquid product, a test run of 4½ hours was carried out.

Feedstock

The feedstock consisted of commercial white paraffin wax with a molecular weight range of 310–530. The average molecular weight of the wax was 375, the melting range 52°–54° C, the boiling range 160°–250° C at 1 mm mercury, and the density (at 70° C) 0·7719. The oil content of the wax, determined as described below, was <1 per cent wt.

Method of Analysis

250 grams of each reaction product was distilled at atmospheric pressure to 300° C and the amount of cracked products boiling below 300° C was determined quantitatively. The reproducibility of the distillations was about 1 per cent wt.

50 grams of each distillation residue was dissolved in warm methyl ethyl ketone, the weight ratio being 1 : 5, and the solution slowly stirred and cooled to −20° C, allowing the wax to crystallize. The solidified mixture was filtered at −20° C by suction, using a filter which was kept at −20° C. The separated wax cake, containing some occluded oil, was treated in the same way as the residue. The two filtrates thus obtained were freed of methyl ethyl ketone by distilling off the solvent at reduced pressure, followed by stripping the last traces with nitrogen at room temperature and 10 cm mercury. After weighing, the two oil portions were combined and the oil yield, defined as the weight percentage oil in the reaction product, calculated. The reproducibility of the values of the oil yield was about 1 per cent wt.

The pour points and viscosity indexes of the obtained oils were determined according to the ASTM method D97–47 and the ASTM method D567–53 respectively. The temperature dependence of the viscosity of the oils was also determined by using a new method [11] based on the relationship:

$$\log \nu = \frac{A}{T^x} + B$$

where ν = kinematic viscosity in cS;
T = absolute temperature in ° K;
A, B, and x are constants.

Preparation of Catalysts and Reaction Conditions

Table I gives a survey of the catalysts used in this investigation and the conditions under which they were tested. In the third and fifth column of this table the concentration (per cent wt) is based on dry alumina. These figures were calculated from the added amounts of $H_2PtCl_6.6H_2O$ and HCl in the catalyst preparation.

The catalysts may be classified in the following groups according to their preparation.

Platinum Oxysulphide–Alumina–Halogen Catalysts [7] (Catalysts Nos. 3, 4, 5, 6, 8, 9, 15)

This catalyst type was used for a major part of the work and was prepared by the following procedure.

1000 grams of aluminium *iso*propylate [8] was made from aluminium and dry *iso*propyl alcohol, and hydrolized in 5 litres of boiling water, while stirring intensively. The required amount of halogen was slowly added to the warm stirred suspension in the form of a concentrated halogen acid. A separate solution of the desired amount of chloroplatinic acid in water (1 per cent wt) was prepared and hydrogen sulphide passed through the solution. The obtained platinum sulphide solution was thoroughly mixed with the warm aluminium hydroxide suspension and the combined mixture oxidized with hydrogen peroxide (50 ml of 30 per cent H_2O_2). After evaporating the water, the resulting paste was dried at 90° C for 14 hours, next heated at 160° C for 14 hours, and finally calcined in an air stream at 600° C for 12 hours. The resulting catalyst was broken into pieces, if necessary, and 300 ml of particles with dimensions ranging from 3 to 4 mm were selected for use in the experiments.

Platinum Sulphide–Alumina–Halogen Catalysts (Catalysts Nos. 11 and 12)

The two identical catalysts were prepared in the same way as those above, but without the oxidation step.

Alumina–Halogen Catalyst (Catalyst No. 2)

This catalyst was prepared as mentioned above, but without the addition of platinum sulphide and the oxidation step.

Alumina (Catalyst No. 1)

This catalyst was prepared as mentioned above, but without the additions of platinum sulphide, halogen, and the oxidation step.

Platinum–Commercial Alumina–Halogen Catalyst (Catalyst No. 7)

Commercial activated alumina in powder form (Hopkins and Williams) was stirred with an excess of was dried at 100° C for 16 hours and impregnated with a dilute solution of chloroplatinic acid and hydrochloric acid in the desired amounts. After drying at 90° and 180° C the catalyst was heated at 520° C for 2 hours.

Cobalt–Molybdate–Alumina Catalyst (Catalyst No. 14)

An aluminium hydroxide suspension was prepared by hydrolizing 1000 grams of aluminium *iso*propylate in 5 litres of boiling water. After cooling, a solution of cobalt nitrate was added to the stirred suspension. Cobalt molybdate was then precipitated by adding a solution of ammonium paramolybdate in dilute ammonia, and the mixture filtered. The filter cake

TABLE I

Composition of Catalysts and Reaction Conditions

Experiment No.	Catalyst					Conditions							
	No.	Hydrogenation component	Support material	Halogen	Remarks	Time, hours	Temperature, °C	Pressure, atm	Weight hourly space velocity, kg/l/hr	Gas-rate, nL, H_2/kg	Contact time, seconds	Molar ratio, H_2/wax	Partial pressure of paraffin wax
1	1	—	Al_2O_3	—		5½–10	435	51	0·97	5,600	9·7	94	0·54
2	2	—	Al_2O_3	2·0% Cl		5½–10	435	51	0·97	5,600	9·7	94	0·54
3	3	0·1% Pt	Al_2O_3	0·1% Cl		5½–10	435	51	0·97	5,600	9·7	94	0·54
4	4	0·1% Pt	Al_2O_3	2·1% Cl		5½–10	435	51	0·97	5,600	9·7	94	0·54
5	5	0·1% Pt	Al_2O_3	5·1% Cl		5½–10	435	51	0·97	5,600	9·7	94	0·54
6	6	0·1% Pt	Al_2O_3	0·1% Cl, 2·0% F		5½–10	435	51	0·97	5,600	9·7	94	0·54
7	7	0·1% Pt	Al_2O_3	2·1% Cl	Commercial alumina	5½–10	435	51	0·97	5,600	9·7	94	0·54
8	8	0·2% Pt	Al_2O_3	1·8% Cl		5½–10	435	51	0·97	5,600	9·7	94	0·54
9	9	0·4% Pt	Al_2O_3	2·4% Cl		5½–10	435	51	0·97	5,600	9·7	94	0·54
10	10	0·1% Pt	SiO_2	2·1% Cl		5½–10	435	51	0·97	5,600	9·7	94	0·54
11	11	0·1% Pt	Al_2O_3	2·1% Cl	Unoxidized	5½–10	435	51	0·97	5,600	9·7	94	0·54
12	12	0·1% Pt	Al_2O_3	2·1% Cl	Unoxidized	5½–10	435	51	0·97	5,600	9·7	94	0·54
13	3	0·1% Pt	Al_2O_3	0·1% Cl	1 × regenerated	5½–10	435	51	0·97	5,600	9·7	94	0·54
14	3	0·1% Pt	Al_2O_3	0·1% Cl	1 × regenerated	12–16½	425	51	0·98	5,590	9·7	94	0·54
15	4	0·1% Pt	Al_2O_3	2·1% Cl	1 × regenerated	5½–10	425	51	0·98	5,590	9·7	94	0·54
16	4	0·1% Pt	Al_2O_3	2·1% Cl	2 × regenerated	5½–10	415	51	1·00	5,530	9·8	93	0·54
17	13	10% MoO_3	Al_2O_3	0·5% F		5½–10	435	51	0·97	5,600	9·7	94	0·54
18	14	33% $CoMoO_4$	Al_2O_3	—		5½–10	435	51	0·97	5,600	9·7	94	0·54
19a	4	0·1% Pt	Al_2O_3	2·1% Cl	3 × regenerated	2½–3½	435	51	0·97	5,600	9·7	94	0·54
19b	4	0·1% Pt	Al_2O_3	2·1% Cl	3 × regenerated	3½–4½	435	51	0·97	5,600	9·7	94	0·54
19c	4	0·1% Pt	Al_2O_3	2·1% Cl	3 × regenerated	4½–5½	435	51	0·97	5,600	9·7	94	0·54
19d	4	0·1% Pt	Al_2O_3	2·1% Cl	3 × regenerated	5½–10	435	51	0·97	5,600	9·7	94	0·54
19e	4	0·1% Pt	Al_2O_3	2·1% Cl	3 × regenerated	10–11	435	51	0·97	5,600	9·7	94	0·54
19f	4	0·1% Pt	Al_2O_3	2·1% Cl	3 × regenerated	11–12	435	51	0·97	5,600	9·7	94	0·54
19g	4	0·1% Pt	Al_2O_3	2·1% Cl	3 × regenerated	12–13	435	51	0·97	5,600	9·7	94	0·54
19h	4	0·1% Pt	Al_2O_3	2·1% Cl	3 × regenerated	13–14	435	51	0·97	5,600	9·7	94	0·54
19i	4	0·1% Pt	Al_2O_3	2·1% Cl	3 × regenerated	14–15	435	51	0·97	5,600	9·7	94	0·54
20a	15	0·1% Pt	Al_2O_3	2·1% Cl		4–8	410	52	1·04	5,260	10·1	88	0·58
20b	15	0·1% Pt	Al_2O_3	2·1% Cl		36–40	433	32	0·99	3,210	10·3	54	0·58
20c	15	0·1% Pt	Al_2O_3	2·1% Cl		52–56	435	72	1·01	7,250	10·1	121	0·59
20d	15	0·1% Pt	Al_2O_3	2·1% Cl		60–64	435	102	0·96	10,910	10·1	183	0·56
20e	15	0·1% Pt	Al_2O_3	2·1% Cl		76–80	455	52	0·89	5,060	16·4	61	0·82
20f	15	0·1% Pt	Al_2O_3	2·1% Cl		100–104	450	52	1·00	5,150	10·2	86	0·60

1·0N hydrochloric acid for 30 minutes and washed with distilled water till the decantate was Cl-free. The purified alumina was dried, heated at 600° C for 2 hours, and impregnated with a dilute solution of chloroplatinic acid and hydrochloric acid in the desired amounts. After drying at 90° and 180° C the catalyst was pelleted (3 × 5 mm) and the pellets heated in an air stream at 600° C for 2 hours.

Platinum–Silica–Halogen Catalyst[9] (Catalyst No. 10)

Commercial granular silica (Gembo) of about 3–4 mm dimensions was boiled with an excess of 4·0N of hydrochloric acid and washed with distilled water till the decantate was Cl-free. The purified silica was re-slurried in an excess of distilled water and filtered again; this operation was repeated once more. The filter cake was then dried at 100° C for 48 hours and calcined in a nitrogen stream at 600° C for 12 hours.

The added amounts of $Co(NO_3)_2.6H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ corresponded to 33 per cent wt $CoMoO_4$ based on dry alumina.

Molybdenum–Alumina–Fluor Catalyst[10] (Catalyst No. 13)

Aluminium chloride was hydrolized with dilute ammonia and the suspension heated to 80° C. The precipitate was filtered and washed with dilute

ammonia till the filtrate was Cl-free. The filter cake was then re-slurried and thoroughly mixed with a dilute solution of hydrofluoric acid and subsequently with a solution of ammonium molybdate. The resulting mass was dried and calcined in a nitrogen stream at 500° C for 2 hours. The amounts of ammonium paramolybdate and hydrofluoric acid corresponded to 10 per cent wt MoO_3 and 0·5 per cent wt F based on dry alumina.

Regenerated Catalysts

The regeneration of used catalysts (Catalysts Nos 3 and 4) was carried out by heating the catalyst in a nitrogen stream to about 500° C. The nitrogen was then carefully diluted with air; the carbonaceous deposits on the catalyst surface being burnt. During the regeneration the temperature was kept below 550° C. When the catalyst had regained its original colour the temperature was raised to 600° C and the catalyst heated in an air stream for 2 hours more.

DISCUSSION OF THE RESULTS

Relationship between the Isomerization and Cracking Reaction

The obtained reaction products may be regarded as *pseudo* three-component systems of which the components are: oil, unconverted wax, and cracked products. The percentages of these components are shown in Table II and plotted in a triangular diagram (right-angled) of the isosceles type (Fig 1). In this diagram the ordinate represents the course of selective isomerization, while the abscissa represents cracking of the paraffin wax. It can be seen from Fig 1 that it is possible to draw a curve through the points representing the experiments that are carried out with the platinum type catalysts, while the points representing experiments with other catalysts do not lie on the curve. It has been found that the curve may be represented by an equation of the second degree, namely,

$$y = \frac{x(1-x)}{a+bx} \quad . \quad . \quad . \quad . \quad (1)$$

in which y and x are the two co-ordinate lines of the diagram, while a and b are constants. The values of a and b are respectively 0·040 and 0·995. Equation (1) represents a hyperbola of which the equations of the asymptotes are $x = -a/b$ and $bx + b^2y = a + b$. The curve in the diagram is therefore a part of one branch of the hyperbola.

In a study concerning selectivity problems in chemical reactions * it will be shown that equation (1) can be applied more generally to complex simultaneous reactions occurring in processes different from those discussed in this paper.

The reaction products are also regarded as *pseudo* three-component systems, the components being unconverted products, desired products, and side products. In every case it was found that the concentration change of the three chosen components, as a result of the variations of one reaction variable, can be approximated by equation (1).

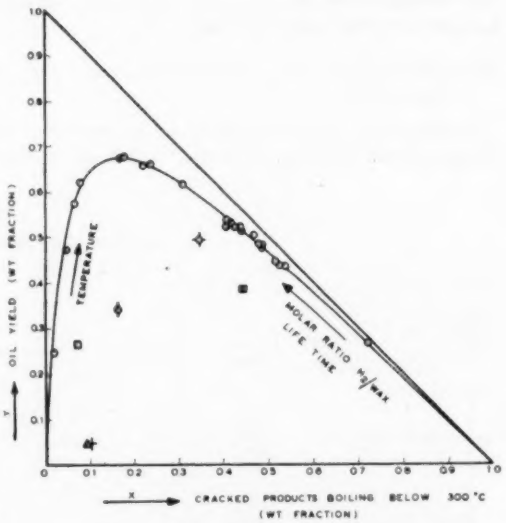

FIG 1

PRODUCT DISTRIBUTION OF REACTION PRODUCTS

⊙ Experiments with platinum type catalysts

△ + ⊡ ⬡ ⌖ □ Experiments with other catalysts

The Influence of Reaction Variables on the Product Distribution

The course of the curve can be followed in different directions by altering reaction variables as, for example, temperature, life time of the catalyst, and molar ratio H_2/wax. This means that the values of a and b in this case are not affected by these reaction variables. The directions are indicated in Fig 1 and shown in detail for series of comparable experiments in Figs 2 (*a*)–(*d*). From Fig 2 (*a*) it appears that the distribution curve is followed in a direction from left to right at increasing reaction temperature. In Figs 2 (*b*) and (*c*) the results of some experiments of an earlier investigation [6] are shown. These experiments differ from the present series in that the test runs were carried out successively with the same catalyst. From Fig 2 (*b*) it can be seen that the course of the curve is followed in a

* This subject will be dealt with in a separate paper.

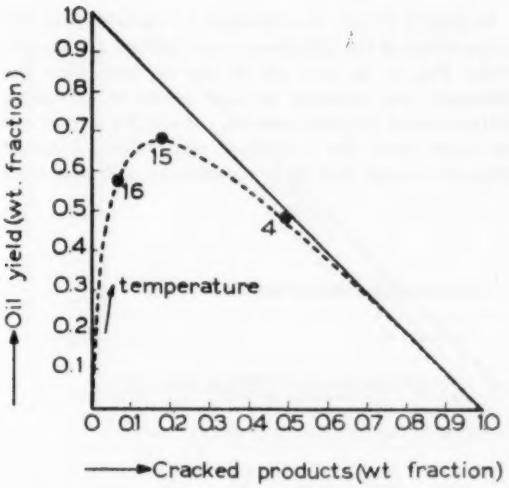

FIG 2 (*a*)

VARIATION OF REACTION TEMPERATURE (415°–425°–435° C)

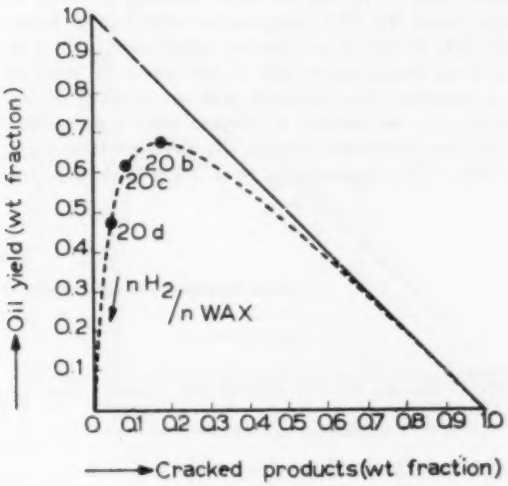

FIG 2 (*b*)

VARIATION OF MOLAR RATIO H_2/WAX (nH_2/n WAX : 54–121–183)

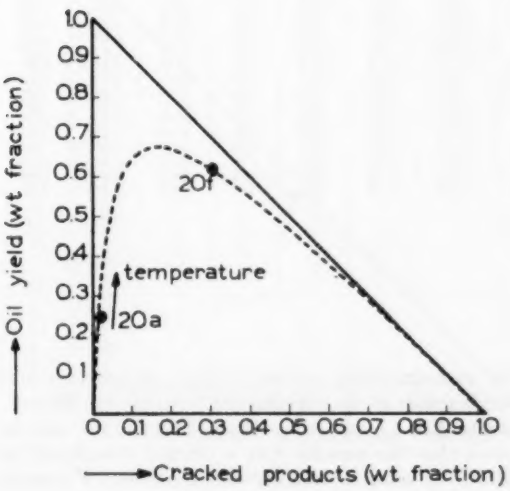

FIG 2 (*c*)

VARIATION OF REACTION TEMPERATURE (410°–450° C)

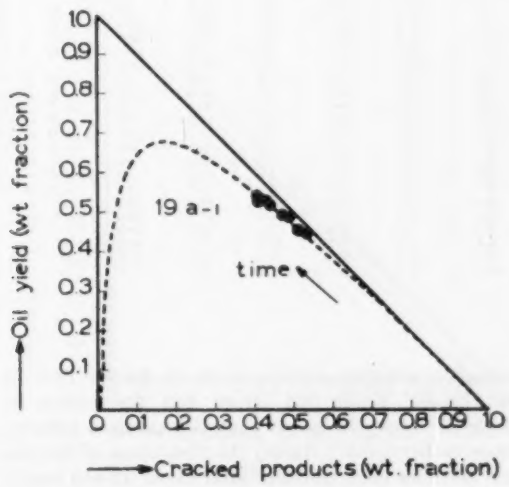

FIG 2 (*d*)

VARIATION OF TIME (RUN HOURS 0–15)

FIG 2 (*a*)–(*d*)

THE INFLUENCE OF SOME REACTION VARIABLES ON THE PRODUCT DISTRIBUTION

direction from right to left at increasing molar ratio H_2/wax. In Fig 2 (*c*) the temperature influence is shown again. It can be noted that the position of experiment No. 20*f* (temperature 450° C, run hours 100–104) is left from that of experiment No. 4 in Fig 2 (*a*) (temperature 435° C, run hours 5½–10). It can therefore be concluded that an increase in the lifetime of the catalyst is coupled with a movement along the distribution line in the direction from right to left. This appears also from Fig 2 (*d*), where the change in catalyst activity is shown for the first 15 run hours. From this figure and the values in Table II it can be noted that the catalyst activity drops rather quickly during the first hours of the run and becomes more constant after about 10 run hours. Furthermore, it can be noted from Table II that a regenerated catalyst has about the same activity as a fresh catalyst (Experiments Nos 3 and 13).

From the given examples it is clear that knowledge of the position of the distribution curve in the diagram, connected with the indication of the influence of reaction variables, permits an easy adjusting of the reaction variables to obtain the optimal product distribution (67 per cent wt oil, 15–20 per cent wt cracked products, 18–13 per cent wt unconverted wax).

The Influence of Variations in the Preparation of the Platinum Type Catalyst

In Figs 3 (*a*)–(*d*) the influence of variations in the preparation of the platinum type catalyst are shown. From Figs 3 (*a*) and (*b*) it can be seen that the platinum type catalyst is more active at increasing platinum and halogen content. From Fig 3 (*c*) it can be noted that the oxidation step in the catalyst preparation has only little significance and that both the reproducibility of the catalyst preparation and performance of the experiments is satisfying (Experiments Nos 11 and 12). From Fig 3 (*d*) it can be noted that the paraffin wax is cracked completely at 435° C by using a catalyst with 2 per cent F instead of 2 per cent Cl.

TABLE II

Hydro-isomerization of Paraffin Wax. Properties of Reaction Products

Experiment No.	Reaction product distribution					Pour point of the oil, °C	Viscosity in cS (ν)				Viscosity index	F.V.T.I. method		
	Cracked material, % wt	Oil yield, % wt			Solid material, % wt		20° C	100° F (37·8° C)	70° C	210° F (99·9° C)		ν_{20}	$\log \frac{\nu_{20}}{\nu_{99}} = \frac{}{\text{F.V.T.I.}}$	x
		1st extract	2nd extract	Total										
1	9·2	3·2	1·7	4·9	85·9	—	—	—	—	—	—	—	—	—
2	10·2	3·5	1·5	5·0	84·8	—	—	—	—	—	—	—	—	—
3	46·7	48·0	2·2	50·2	3·1	−32	14·08	7·878	3·729	2·285	113	14·08	0·577	3·38
4	47·8	46·2	2·0	48·2	4·0	−28	13·88	7·868	3·704	2·302	117	13·88	0·574	2·98
5	53·8	42·2	1·3	43·5	2·7	−26	13·50	7·513	3·577	2·211	111	13·50	0·570	3·28
6	100·0	—	—	—	—	—	—	—	—	—	—	—	—	—
7	7·0	20·4	5·8	26·2	66·8	—	15·90	9·085	4·311	2·656	145	15·90	0·567	2·95
8	48·3	43·6	3·7	47·3	4·4	−28	14·24	7·997	3·763	2·317	115	14·24	0·578	3·19
9	72·1	26·1	0·7	26·8	1·1	−35	12·71	7·212	3·428	2·133	106	12·71	0·569	3·14
10	16·2	27·5	6·4	33·9	49·9	−20	16·22	9·097	4·270	2·620	137	16·22	0·580	3·20
11	43·7	50·5	1·7	52·2	4·1	−28	14·30	8·003	3·766	2·317	115	14·30	0·579	3·28
12	43·8	50·8	1·9	52·7	3·5	−23	14·18	7·952	3·762	2·306	115	14·18	0·576	3·33
13	48·8	45·4	2·8	48·2	3·0	—	13·43	7·600	3·618	2·226	111	13·43	0·570	3·23
14	21·9	59·8	5·8	65·6	12·5	−23	14·99	8·462	3·994	2·445	125	14·99	0·574	3·14
15	17·6	58·5	9·0	67·5	14·9	−23	16·32	9·025	4·211	2·554	127	16·32	0·588	3·39
16	6·5	39·7	17·5	57·2	36·3	−22	19·06	10·483	4·780	2·863	137	19·06	0·601	3·13
17	34·5	45·3	4·0	49·3	16·2	−21	14·08	7·979	3·791	2·351	124	14·08	0·570	3·16
18	44·0	31·7	6·7	38·4	17·6	—	13·26	7·572	3·621	2·216	110	13·26	0·564	3·09
19a	51·4	43·0	1·6	44·6	4·0	−28	13·67	7·722	3·660	2·271	116	13·67	0·572	3·19
19b	52·6	42·6	1·2	43·8	3·6	−28	13·15	7·444	3·560	2·207	113	13·15	0·567	3·30
19c	48·4	46·7	1·4	48·1	3·5	−25	13·63	7·668	3·644	2·249	115	13·63	0·573	3·33
19d	47·8	46·2	2·0	48·2	4·0	−28	13·88	7·868	3·704	2·302	117	13·88	0·574	3·00
19e	41·5	50·5	2·5	53·0	5·5	−24	14·29	8·066	3·813	2·337	117	14·29	0·574	3·16
19f	44·0	49·2	1·9	51·1	4·9	−28	14·21	8·117	3·834	2·317	110	14·21	0·569	2·88
19g	42·4	50·5	1·8	52·3	5·3	−21	13·84	7·890	3·732	2·306	117	13·84	0·569	2·95
19h	40·7	51·6	1·9	53·5	5·8	−22	14·04	8·020	3·768	2·316	114	14·04	0·571	2·78
19i	41·2	49·5	2·5	52·0	6·8	−25	14·05	7·926	3·766	2·314	118	14·05	0·572	3·27
20a	2·0	15·1	9·5	24·6	73·4	—	—	—	—	—	—	—	—	—
20b	16·7	61·7	5·6	67·3	16·0	—	—	—	—	—	—	—	—	—
20c	7·7	42·8	19·2	62·0	30·3	—	—	—	—	—	—	—	—	—
20d	4·6	31·2	15·9	47·1	48·3	—	—	—	—	—	—	—	—	—
20e	23·5	56·0	10·1	66·1	10·4	—	—	—	—	—	—	—	—	—
20f	30·7	58·1	3·3	61·4	7·9	—	—	—	—	—	—	—	—	—

Comparison of Catalysts

The experimental fact that for a given catalyst the variation of any reaction variable is connected with concentration changes in the products according to equation (1) has an interesting consequence. Suppose that one experiment is carried out and that the result is plotted in the diagram. The function is then not yet determined and an infinite amount of hyperbolas, going through the angular points ($x = 0$, $y = 0$),

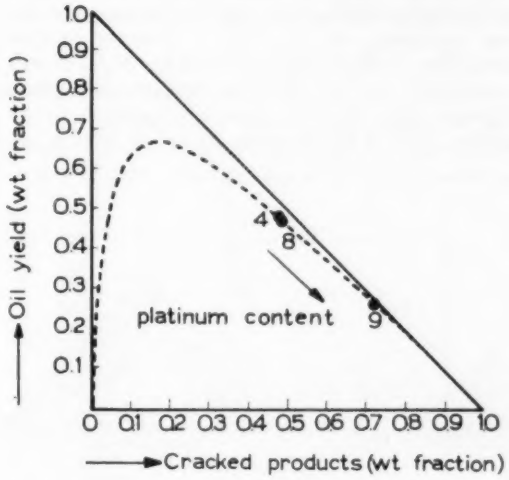

FIG 3 (*a*)

INFLUENCE OF PLATINUM CONTENT OF THE CATALYST
(0·1–0·2–0·4 wt-% Pt)

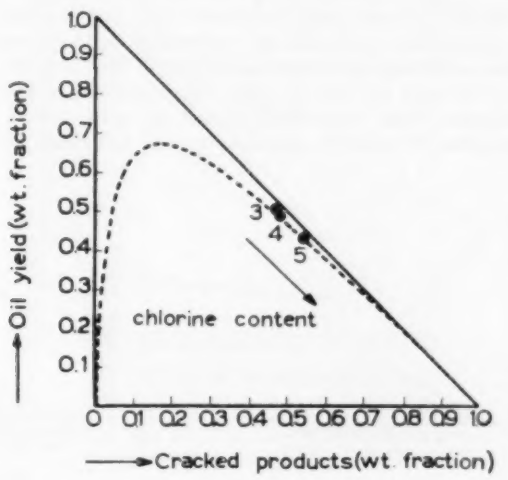

FIG 3 (*b*)

INFLUENCE OF CHLORINE CONTENT OF THE CATALYST
(0·1–2·1–5·1 wt-% Cl)

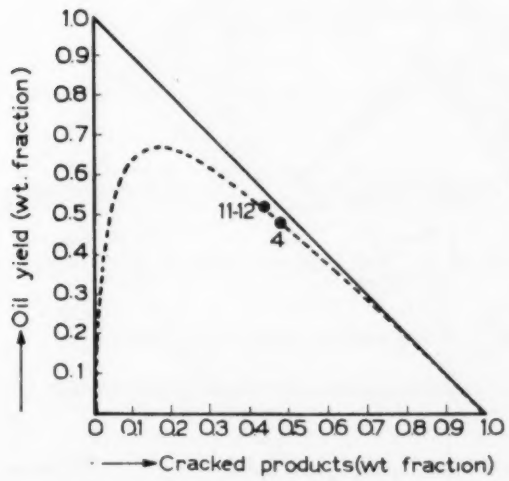

FIG 3 (*c*)

INFLUENCE OF THE OXIDATION STEP IN THE CATALYST PREPARATION

EXPT NO. 4—OXIDIZED CATALYST
EXPTS NOS. 11 AND 12—UNOXIDIZED CATALYSTS

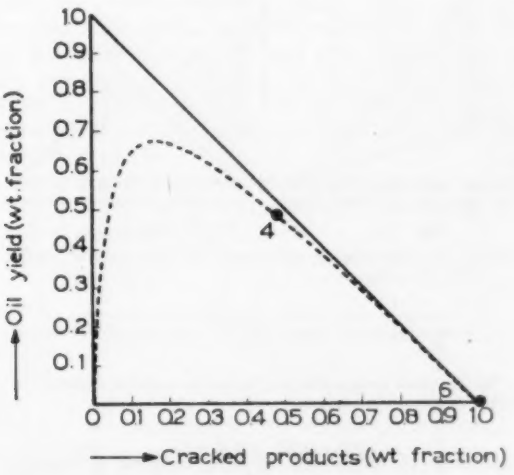

FIG 3 (*d*)

INFLUENCE OF THE KIND OF COMBINED HALOGEN IN THE CATALYST

EXPT NO. 6—2 WT-% F

FIG 3 (*a*)–(*d*)

THE INFLUENCE OF SOME VARIATIONS IN THE PREPARATION OF THE PLATINUM TYPE CATALYST

($x = 1$, $y = 0$) and the experimental point, are still possible. It can easily be shown that the limiting hyperbolas of the bundle are represented by two lines drawn through the experimental point from ($x = 0$, $y = 0$) and ($x = 1$, $y = 0$) respectively. In the diagram these two lines enclose an area, which includes all possible reaction courses according to equation (1), when one reaction variable is changed with respect to the conditions of the experiment. The picture thus obtained covers numerous conditions and can serve as a base of comparison. In Fig 4 (*a*)–(*g*) the predicted areas are shown for several investigated catalysts, tested at identical conditions. By comparing the different areas to each other, the following catalysts may be disqualified by reason of the result of one experiment.

Al_2O_3	Fig 4 (*a*)
Al_2O_3–Cl	Fig 4 (*b*)
Pt–SiO_2–Cl	Fig 4 (*c*)
Pt–commercial Al_2O_3–Cl . .	Fig 4 (*d*)

$CoMoO_4$–Al_2O_3 (Fig 4 (*e*)), MoO_3–Al_2O_3–F (Fig 4 (*f*)), and Pt–Al_2O_3–Cl (Fig 4 (*g*)) can be considered as the most promising of the series. However, in all probability, $CoMoO_4$–Al_2O_3 and MoO_3–Al_2O_3–F will be inferior to the platinum type catalyst. To obtain a sharper differentiation a second experiment, *e.g.* at another reaction temperature, should be carried out with $CoMoO_4$–Al_2O_3 and MoO_3–Al_2O_3–F. The values of a and b can then be evaluated and the corresponding hyperbolas constructed and compared to that of the platinum type catalyst.

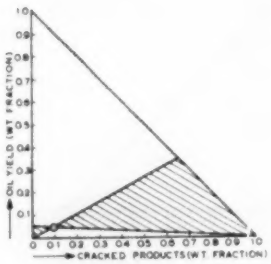

FIG. 4 (*a*)
EXPT NO. 1. Al_2O_3 CATALYST

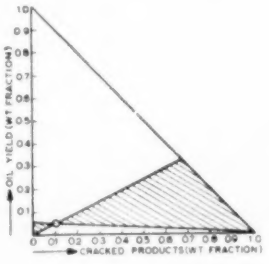

FIG 4 (*b*)
EXPT NO. 2. Al_2O_3–Cl CATALYST

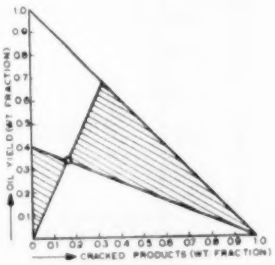

FIG 4 (*c*)
EXPT NO. 10. Pt–SiO_2–Cl CATALYST

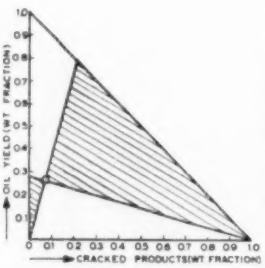

FIG 4 (*d*)
EXPT NO. 7. Pt-COMMERCIAL Al_2O_3–Cl CATALYST

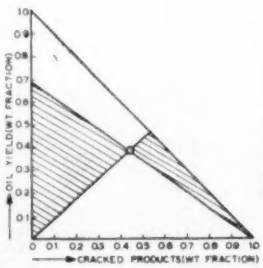

FIG 4 (*e*)
EXPT NO. 18. $CoMoO_4$–Al_2O_3 CATALYST

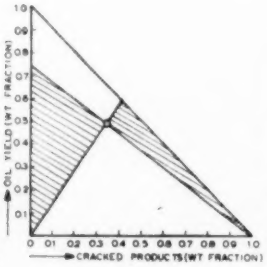

FIG 4 (*f*)
EXPT NO. 17. MoO_3–Al_2O_3–F CATALYST

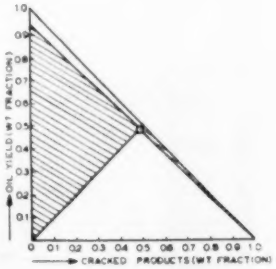

FIG 4 (*g*)
EXPT NO. 4. Pt–Al_2O_3–Cl CATALYST

FIG 4 (*a*)–(*g*)
COMPARISON OF CATALYSTS AT A STANDARD CONDITION (435° C, 51 ATM PRESSURE, WHSV = 0·97, MOLAR RATIO H_2/WAX = 94)

The hatched areas include all possible reaction courses according to equation (1), when one variable is changed with respect to the standard condition.

Summarizing, the authors believe that the method followed in comparing the action of the catalysts, including:

(1) the conception of *pseudo* three-component systems (unconverted, desired, and side products);

(2) the plotting of reaction courses in a triangular diagram;

(3) the application of equation (1);

can be developed into a more general, efficient method

for the screening of catalysts and the evaluation of chemical process reactions in which selectivity is involved.

Quality of the Products

In the experimental part of this paper it was described that the dewaxing operation was carried out in two steps. In Fig 5 the amounts of residue in

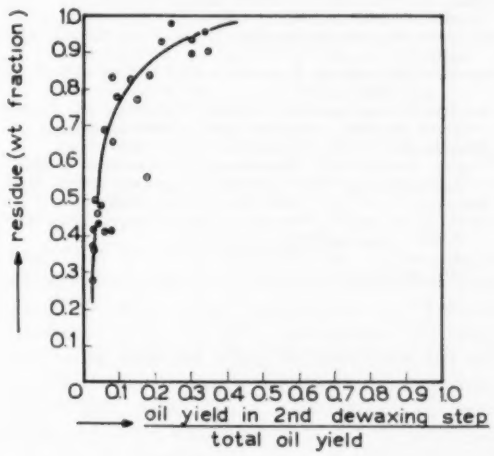

Fig 5

TWO-STAGE DEWAXING OF THE DISTILLATION RESIDUES

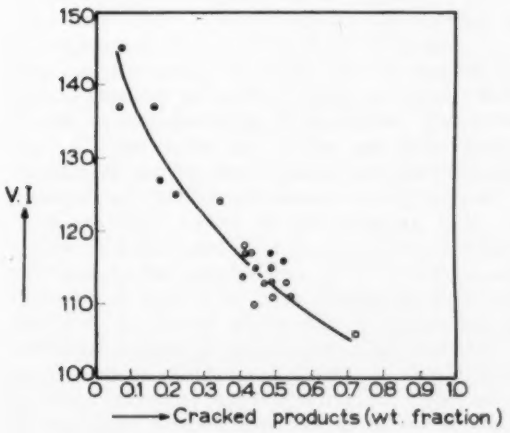

Fig 6

VISCOSITY INDEX OF THE OBTAINED OILS AS FUNCTION OF THE WEIGHT FRACTION OF CRACKED PRODUCTS

the reaction products (per cent wt) are plotted against the amounts of oil obtained in the second dewaxing step (per cent of total oil yield). At optimal conditions (per cent wt cracked material = 10–20) about

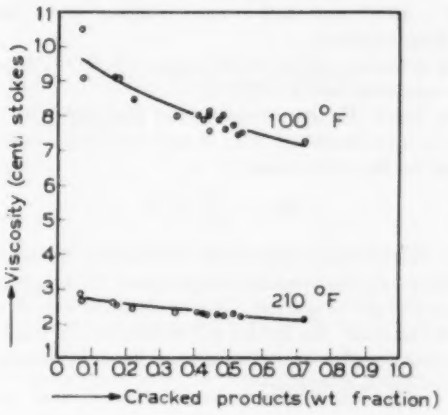

Fig 7

VISCOSITY OF THE OBTAINED OILS AS FUNCTION OF THE WEIGHT FRACTION OF CRACKED PRODUCTS

80 per cent of the oil is separated in the first dewaxing step and 20 per cent in the second.

As regards the quality of the oils obtained, it is clear from Table II and Fig 6 that the viscosity indexes of the oils vary between 105 and 145, and that the viscosity index decreases when cracking increases. At optimal conditions the viscosity indexes of the oils lie between 125 and 135. The values of the viscosities of the oils are given in Fig 7, from which it is apparent that the viscosity of the oils obtained at optimal conditions is 9·0 cS at 100° F and 2·6 cS at 210° F.

The values of the pour points of the oils are shown in Table II and are plotted against the percentage of cracked material in Fig 8.

The pour points of the oils vary between −21°

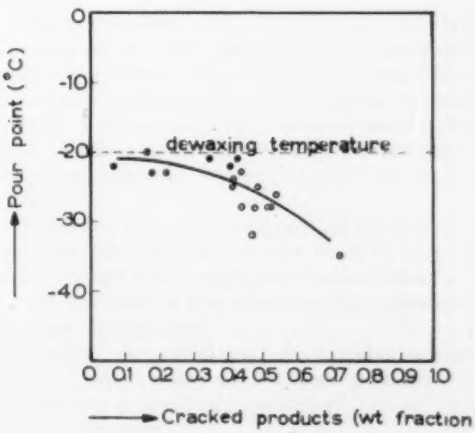

Fig 8

POUR POINT OF THE OBTAINED OILS AS FUNCTION OF THE WEIGHT FRACTION OF CRACKED PRODUCTS

and $-35°$ C and they become slightly lower when cracking increases.

At optimal conditions the pour points of the oils are somewhat below $-20°$ C.

In Table II the temperature dependence of the oils is also described with a new method, which is based on the relationship:

$$\log \nu = \frac{A}{T^x} + B$$

In this formula ν represents the kinematic viscosity of the oil at the absolute temperature $T°$ K, while A, B, and x are constants. For a detailed description of the method, the reader is referred to the paper in question.[11] The classification of the oils according to this method includes:

(1) The calculation of the value of x from the viscosity data at 20°, 38°, and 70° C.

(2) The calculation of the values: $\log \frac{\nu_{20}}{\nu_{70}}$ which are a practical substitute of the constant A.

(3) The presentation of viscosity data at, *e.g.* 20° C, which are a substitute for the constant B.

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THE CHEMICAL CONSTITUTION OF THE HIGHER "NAPHTHENIC ACIDS" *

By J. KNOTNERUS†

SUMMARY

The investigation described was concerned with the constitution of "naphthenic acids" originating from the lubricating oil distillates of a Venezuelan crude oil.

The acids, after purification, were converted into their methyl esters and fractionated; the fractions were converted into neutral compounds by reduction via the primary alcohols and iodides ($R{\cdot}COOCH_3 \longrightarrow R{\cdot}CH_3$). The neutral derivatives were separated by chromatography and thermal diffusion and analysed by methods in use in present-day oil constitution work.

It could be concluded from the results that the higher "naphthenic acids" are carboxylic acids based not only on substituted naphthenes, but also on most of the other compounds present in lubricating oils, namely, mono-aromatics, di-aromatics, and sulphur compounds (*e.g.* benzothiophenes). Acids derived from poly-aromatics could not, however, be detected.

The name "naphthenic acids" is hence inappropriate, and it would be better to speak of "petroleum acids."

INTRODUCTION

NAPHTHENIC acids are obtained in oil refineries as subsidiary products in the manufacture of hydrocarbon distillates. They are used, as such or in the form of their salts with the alkali or heavy metals, for a variety of purposes, *e.g.* wetting agents, emulsifiers or demulsifiers, paint driers, preservatives for textile goods and wood, and as additives for EP lubricants.

It may be said that only the naphthenic acids in the lower range of molecular weights have been studied extensively as individual compounds. The commercial products referred to above were formerly made mainly from the acids within this range (namely, from those occurring in the kerosine and light gas oil hydrocarbon fractions); there exists at present, however, an increasing tendency also to employ for various purposes the acids of higher molecular weight present in the lubricating oil distillates. The structure of these acids had so far not been clearly established, and the investigation here described was undertaken to provide information on this subject.

An excellent review of the previous work on petroleum acids, together with exhaustive references to literature, has recently been given by Lochte and Littmann in their book "The Petroleum Acids and Bases." [1] As stated above, the investigations on individual naphthenic acids were chiefly confined to the lower acids—those up to about C_{10}. It is difficult to isolate individual compounds from the higher acids, so that these must be examined as mixtures, which may at best be separated into a number of type fractions.

The earlier investigations, among which those of Zelinsky [2] and von Braun [3] should be mentioned, gave the impression that the lower naphthenic acids are principally carboxylic acids containing a saturated ring. Acids with a *cyclo*pentane ring seem to predominate in amount, but a number of acids with a C_6 ring also occur. J. Müller and S. von Pilat,[4] however, considered that naphthenic acids of higher molecular weight may also contain aromatic rings, as after reduction of the acids to the corresponding hydrocarbons a considerable difference was found between calculated molecular refractions and those actually observed. Müller and von Pilat did not study the chemical constitution of these hydrocarbons, but investigated the viscosities of the oils obtained after a sulphuric acid treatment of the reduced material.

Goheen,[5] who also converted lub oil naphthenic acids into hydrocarbons, found scarcely any aromatics. On the evidence obtained by the Kurtz–Lipkin method, based on density observations, he believed that these hydrocarbons contained two to three 5-membered rings per molecule. The quantitative conclusions thus arrived at are, however, questionable.[6]

The more recent study of Lochte and co-workers [1] contributes no new feature to the constitution of naphthenic acids. These authors observed that in the lower range both *cyclo*pentyl and *cyclo*hexyl acids are found. Furthermore, they demonstrated definitely that aromatic acids occur in naphthenic acids from Northern California crude, though in low concentrations.

Eilers and Eisma,[7] in studying the emulsification of asphaltic bitumen, showed that the C/H ratio of the acids isolated from a residual bitumen resembled that of the maltenes of this bitumen, thus indicating the presence of aromatics.

Finally, the presence of aromatic-substituted C_{12}–C_{30} fatty acids in bitumen possessing good emulsifying properties is mentioned, but not proved, in a French patent.[8]

* MS received 10 May 1957.

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OUTLINE OF THE PRESENT WORK

The recent rapid development of highly efficient methods of separation and analysis for mineral oil fractions, namely, chromatography, ion exchange, infra-red and ultra-violet analysis, etc., facilitates the investigation of the chemical nature of the petroleum acids.

For a successful application of these new techniques in the present investigation, the acids were first separated from the hydrocarbon or neutral part of the oil fraction. A suitable base material is the alkaline residue obtained on redistilling a wide-range lub oil distillate over caustic soda; this product contains naphthenates and neutral oil in about equal quantities. The acids were then esterified with methanol, since the methyl esters are more amenable to physical separation than the naphthenic acids. Subsequent molecular distillation of the esters produced a number of fractions of increasing molecular weight. In order to establish their chemical constitution, the esters were reduced completely to the hydrocarbons and then subjected to the methods of analysis in use at present.

This scheme of investigation is summarized below:

Alkaline lub oil redistillation residue
↓ treatment with dilute sulphuric acid
Naphthenic acids + neutral oil
↓ percolation through alumina
Naphthenic acids (R·COOH)
↓ esterification with methanol
Methyl esters ($R{\cdot}COOCH_3$)
↓ molecular distillation
Ester fractions
↓ reduction with lithium aluminium hydride
Primary alcohols ($R{\cdot}CH_2OH$)
↓ iodination, followed by reduction with zinc and HCl
Hydrocarbons ($R{\cdot}CH_3$)
↓ percolation through alumina
Type fractions of hydrocarbons.

These type fractions were further investigated with the aid of: (1) elementary, u.v., and i.r. analysis; (2) thermal diffusion; and (3) dehydrogenation.

The mixed naphthenates forming the starting point of the present investigation were produced in refining an oil of Venezuelan origin.

EXPERIMENTAL RESULTS

Separation of Acids

The acids were first freed from their sodium salts by treatment with dilute sulphuric acid; they were then dissolved in benzene and percolated through alumina,* using benzene, benzene–ethanol, and benzene–acetic acid as successive eluents. The results obtained are given in Table I.

TABLE I

Percolation of the Acidic Oil Obtained on Acidification of the Alkaline Distillation Residue

Fraction obtained with the eluent below	Yield, % wt on oil of fraction	Acidity of fraction meq/g
Benzene	30·2	0
Benzene–ethanol (1 : 1) .	13·0	0·008
Benzene–acetic acid (3 : 1) .	53·4	2·68
(Loss)	(3·4)	—

With the benzene–acetic acid mixture a small quantity of alumina was removed from the column, to form soluble aluminium salts with the organic acids. This required a wash of the product with hydrochloric acid. The third fraction proved to contain no unsaponifiable material and may therefore be regarded as a pure naphthenic acid fraction.

Preparation of Methyl Ester Fractions

The third fraction was dissolved in a mixture of pure dry methanol and benzene (4 : 1), the latter being necessary for rendering the mixture homogeneous. Esterification of the acids was effected by introducing dry hydrogen chloride gas. The esters formed were recovered in the normal way in a yield amounting to 80 per cent of theory. The unconverted acids were separated from the esters by chromatography over alumina, the benzene fraction now containing the esters and the benzene–acetic acid fraction the free acids. The unreacted acids were then treated anew with methanol and hydrogen chloride. The total yield of esters amounted to about 95 per cent.

As a normal distillation *in vacuo* was not suitable, the esters were fractionated at a pressure below 10^{-3} mm Hg in a centrifugal cyclic batch molecular still.† Some properties of the fractions collected are shown in Table II. The decrease in density of the distillate fractions with rising molecular weight is parallel to that observed in other ester series of homologous organic acids, *e.g.* in those of the higher fatty acids, where d_{20} of the ethyl esters falls from 0·8710 for caproic acid (C_6) to 0·8615 for lauric acid (C_{12}) and d_{50} of the benzyl esters from 0·9330 for lauric acid to 0·9049 for stearic acid (C_{18}).

The distilled esters, ranging in colour from water-white to yellow, are mobile liquids, in contrast to the acids themselves, which are viscous oils.

* Peter Spence, type H. † Developed by the Distillation Products Industries, Rochester, New York.

Reduction of Methyl Esters to Hydrocarbons

The conversion of the methyl esters into hydrocarbons was achieved in three steps. The esters were reduced with lithium aluminium hydride to the corresponding primary alcohols,[9] which in their turn were converted with hydriodic acid into the iodides; finally, these compounds were reduced with zinc powder and hydrochloric acid. As far as appears from literature, $LiALH_4$ has never before been applied for reducing naphthenic acids, whereas the following steps have been employed previously, amongst others, by Müller and von Pilat.[4]

The yield was nearly 100 per cent; the completeness of the reactions was verified by infra-red analysis, which showed the total disappearance of the carbonyl and subsequently of the hydroxyl absorption bands.

Table III gives some analytical data of the various products.

The distillation residue of the esters was dark in colour. For the further examination, the ester residue was treated with pentane; the soluble portion (81 per cent wt) was reduced.

TABLE II

Properties of Methyl Esters of Naphthenic Acids

Fraction of methyl esters by mol distillation	Yield % wt	Mol weight	d_{20}	n_D^{20}	Viscosity, cS	
					100° F	210° F
Fraction 1	17·8	297	0·9671	1·4834	19·7	3·29
Fraction 2	18·6	325	0·9671	1·4879	34·4	4·45
Fraction 3	18·6	398	0·9661	1·4939	76·0	8·02
Fraction 4	19·3	428	0·9656	1·4979	133·3	10·05
Residue .	24·7	638	1·0076	1·538	5470·0	97·4
Cold trap .	1·0	—	—	—	—	—

Analysis of the Reduction Products

The hydrocarbons from the ester distillate fractions 2 and 4 and the pentane-soluble part of the residue were separated chromatographically over alumina into a number of fractions, whose refractive indices were determined (see Figs 1–3) and u.v. absorption spectra recorded.

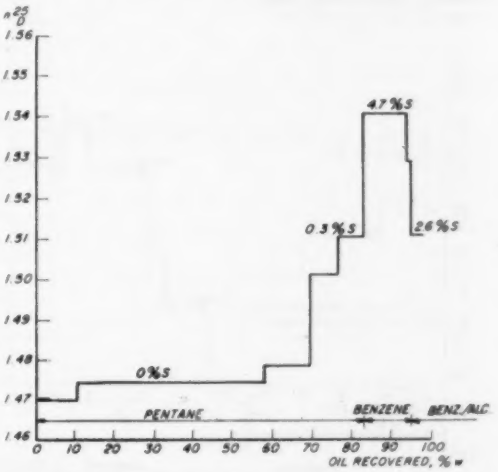

FIG 1

CHROMATOGRAM OF THE REDUCED PRODUCT, EX METHYL ESTER MOL DISTILLATION FRACTION NO. 2
Al_2O_3/oil ratio: 20

TABLE III

Reduction of Esters.

Some Analytical Data of Starting Materials, Intermediate Alcohols, and End Products

Methyl esters				Alcohols				Hydrocarbons		
Fraction No	H/C ratio (atomic)	% S	n_D^{25}	H/C ratio (atomic)		% S	n_D^{25}	H/C ratio (atomic) found	% S	n_D^{25}
				Found	Calc.*					
1	1·708	0·50	1·4834	1·825	1·79	0·55	1·4958	1·82	0·45	1·4830
2	1·72	0·75	1·4879	1·82	1·795	0·8	1·4997	1·82	0·7	1·4880
3	1·715	1·07	1·4939	1·795	1·78	1·1	1·5031	1·79	0·9	1·4930
4	1·72	1·25	1·4979	1·78	1·78	1·3	1·5073	1·78	1·2	1·4975
Residue	1·57	1·94	1·538	—	—	—	—	—	—	1·511

* Calculated from H/C ratios of the esters and their mol weights. On converting alcohols to hydrocarbons the calculated H/C ratios remain unchanged.

The graphs for the refractive indices of the chromatographic fractions are, somewhat surprisingly, very similar to those obtained with a neutral distillate fraction of the same range of molecular weight (Fig 4). In all these four graphs flats are found corresponding to saturates at a refractive index (n_D/25° C) of about

1·475–1·480, to mono-aromatics at 1·50–1·51, to di-aromatics and benzothiophenes in the region of 1·54–1·56; the neutral distillate also produces peaks for polyaromatics and dibenzothiophenes above 1·56 (usually showing no sharp transition from the foregoing), which are absent in the chromatograms of the reduced naphthenic acids.

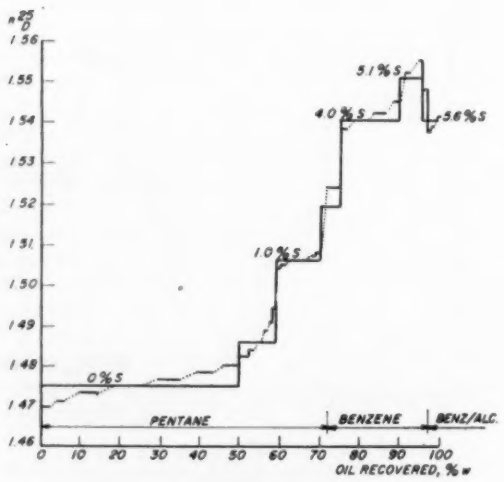

FIG 2

CHROMATOGRAM OF THE REDUCED PRODUCT, EX METHYL ESTER MOL DISTILLATION FRACTION NO. 4
Al_2O_3/oil ratio: 30-recombined fractions

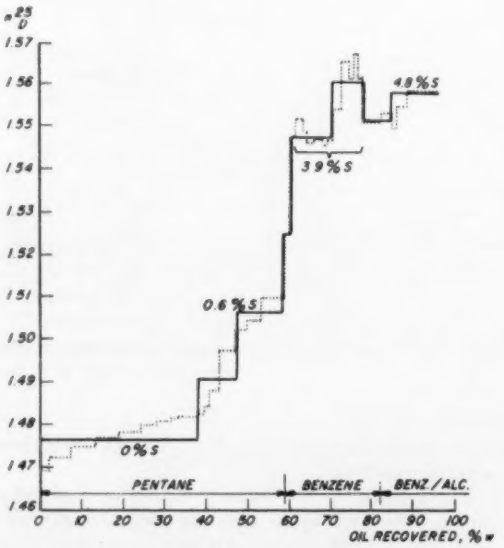

FIG 3

CHROMATOGRAM OF THE REDUCED PRODUCT, EX PENTANE-SOLUBLE PART OF RESIDUAL FRACTION OF METHYL ESTER
Al_2O_3/oil ratio: 30-recombined fractions

U.v. data and elementary analysis of the mono-aromatic fractions of the reduced oils pointed to the presence of naphthenic–aromatic groups with aliphatic

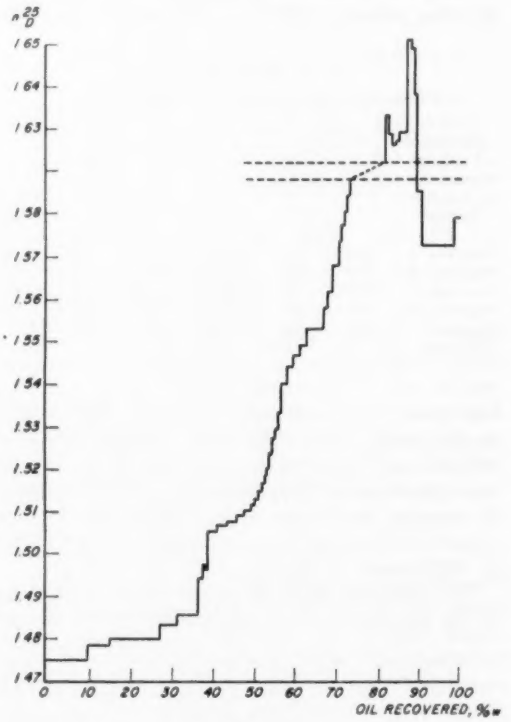

FIG 4

CHROMATOGRAM OF A NEUTRAL UNREFINED OIL (MOL. WT. ABOUT 400) FROM SAME SOURCE

side chains, the general mean formula of which may be written as follows:

From these data, R may be a 5- or 6-carbon ring; C_mH_n represents the total of the alkyl chains, m ranging from about 10 to 20.

The di-aromatic fractions contain sulphur compounds, as appears from the sulphur figures given in the graphs. The u.v. spectra of these fractions indicated the presence of tetra-alkyl-substituted naphthalenes and benzothiophenes.

By combining the evidence obtained from the refractive index data, u.v. spectra, and elementary compositions of the chromatographic fractions, the following estimate was made of the percentages by weight of various types of compounds constituting the reduced oils from the naphthenic acids examined:

The saturated fractions obtained in the chromatographic separations of the reduced oils with molecular weights 281 and 384 were further separated by thermal diffusion in order to obtain information on the ring distribution. With a micro-thermal diffusion column [10] six nearly equal fractions were collected and subjected to elementary analysis. The results given in Table V indicate a separation according to the number of naphthene rings per molecule ranging from about 1·5 to 3.

TABLE IV

Type Distribution of Oils Obtained from Naphthenic Acids

Mol weights of methyl esters	325	428	470
Mol weights of reduced fractions	281	384	*
Saturates, % wt	68	58	45
Mono-aromatics, % wt	15	18	16
Di-aromatics, % wt	6	8	} 23
(Di)benzothiophenes, % wt	5	12	}
(Di)benzothiophenes, (calc. from sulphur content †)	(5·5)	(14)	(23)
Resins, wt %	6	4	16

* From pentane-soluble part of residue.
† Assuming that all sulphur is present in this form.

TABLE V

Analysis of Thermal Diffusion Fractions

Fraction number	Initial material = saturates, derived from ester fraction No. 2, mol weight 281			Initial material = saturates, derived from ester fraction No. 4, mol weight 384		
	n_D^{23}	H/C ratio (atomic)	Ring number	n_D^{23}	H/C ratio (atomic)	Ring number
1	1·4616	1·93	1·7	1·4657	1·96	1·55
2	1·4662	1·91	1·9	1·4693	1·935	1·9
3	1·4710	1·89	2·1	1·4728	1·92	2·1
4	1·4763	1·86	2·4	1·4772	1·865	2·85
5	1·4855	1·81	2·9	1·4837	1·885	2·6
6	1·4938	1·79	3·1	1·4911	1·85	3·05
Average	—	1·875	2·3	—	1·905	2·3
Orig. saturates	1·4748	1·885	2·2	1·4751	1·94	1·8

Fig 5 shows the thermal diffusion diagrams.

Thermal diffusion fractions 2 and 4 (Table V) of both molecular weight series were subjected to a catalytic dehydrogenation in the liquid phase at 200° C with a platinum catalyst.[11] All fractions proved to be convertible into aromatic but to a small extent, namely, 5–8 % wt. In this respect they behave quite similarly to the saturated parts of neutral lub oils.

The fractions obtained by thermal diffusion were examined by i.r. absorption spectrometry. Unfortunately, however, the information provided by this method was not sufficiently definite for indicating the number of 5- or 6-membered rings or the number of substituents per molecule, as was hoped.

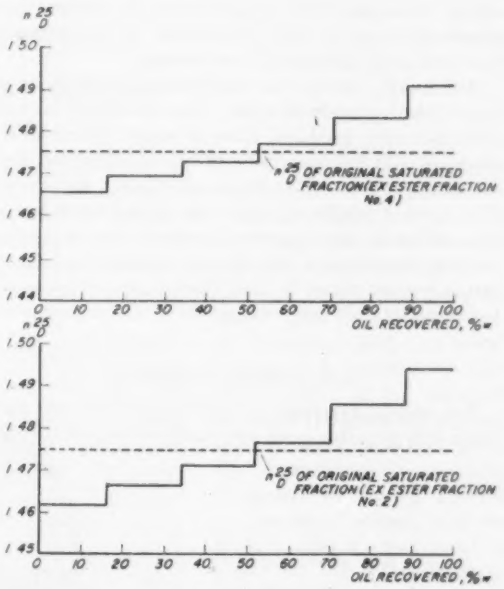

FIG 5

THERMAL DIFFUSION OF THE SATURATED FRACTIONS OF THE REDUCTION PRODUCTS EX METHYL ESTER MOL DISTILLATES NOS 2 AND 4

DISCUSSION AND CONCLUSIONS

Mixed naphthenic acids obtained from the lubricating oil distillate of a Venezuelan crude were purified, fractionated in the form of their methyl esters, and reduced to neutral compounds.

By submitting the latter to separations by chromatography, thermal diffusion, etc., and analysing the fractions by methods such as type analysis, u.v. spectrometry, and elementary analysis, it could be shown that these neutral compounds are very similar in composition to neutral oil fractions of about the same molecular weight from the crude oil. They contain saturates (substituted naphthenes), mono-aromatics, di-aromatics, and sulphur compounds (*e.g.* benzothiophenes). The higher naphthenic acids must therefore be considered as carboxylic acids derived from all these basic structures, and the earlier view that they are principally derivatives of *cyclo*paraffins with alkyl side-chains cannot be maintained.

The name "naphthenic acids" is hence not very appropriate, and the designation "petroleum acids" would be preferable.

Acids based on polyaromatics, containing more than two aromatic rings, were not found in the material investigated, though the corresponding hydrocarbons are present in the neutral lubricating oil. Probably the main cause of this fact is the high molecular weight (boiling point) of the polyaromatic acids,

which prevents their vaporization or causes their decarboxylation in the preparation of the primary lubricating oil distillate in the refinery.

Admittedly, the above conclusions as regards structure of the "petroleum acids" are based only on data obtained with products from a single (Venezuelan) crude oil. It has therefore not been proved that they are also valid for other base materials. Experience with type analyses of crude oils, however, indicates that different oils in general contain very much the same types of compound, though possibly in different ratios (see reference [6]), and there is no evidence for believing that the same will not hold for the petroleum acids.

ACKNOWLEDGMENTS

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OBITUARIES

WALTER AMBROSE WOODROW

1892–1957

We regret to record the death on 26 May 1957 of Walter A. Woodrow, a member of the Institute for thirty-five years.

Mr Woodrow was born in London in May 1892 and spent most of his working life in the petroleum industry. His first industrial experience was with Palmer's Candle Works at Stratford, in 1907–9, following which he became a member of the laboratory staff of The Ragosine Oil Company Ltd at Bow, until in 1911 he joined the Anglo-American Oil Company Ltd (now Esso Petroleum Company Ltd), with whom he remained for thirty-nine years. After a period in the laboratories at Purfleet, he served in the Seaforth Highlanders during the 1914–18 war and then returned to Purfleet, where he was subsequently in charge of the laboratories for some years. In 1929 he transferred to Vauxhall as head of the kerosine and fuel oil section of the Central Laboratories, which had then been established under Dr F. H. Garner. During the 1939–45 war he was in charge of the Vauxhall laboratories, mainly engaged in work for the Petroleum Board. He had, unfortunately, to retire from the Company in 1950 for reasons of health.

He became an Associate of the Royal Institute of Chemistry in 1936 and a Fellow in 1937. In 1922 he joined the Institute of Petroleum and remained closely associated with its work, particularly on standardization matters, for many years. Soon after joining the Institute he was co-opted to the Standardization Sub-Committee on Kerosine and Intermediates, participating in the work which led to the publication of the first edition of "Standard Methods" in 1924. Subsequently he served on many sub-committees and panels of the Standardization Committee, and was chairman of the panel dealing with colour measurement. His great interest was in kerosine, and his work contributed greatly to the development of the standard methods for assessing burning quality and smoke point. He contributed a number of papers to the *IP Journal* on kerosine, colour, and related subjects, and read a paper on the "Development of Methods of Measuring Tendency to Smoke" at the first World Petroleum Congress in 1933. Mr Woodrow was one of a band of quiet, unassuming workers who, in the early years of the Institute, laid the foundations of its standardization work and helped to establish the Institute as a recognized body in this field. His interest in the work of the Institute continued throughout his career.

His colleagues, both in his own company and in other organizations, will remember the cheerful, willing way in which he would always help or co-operate and also his very real contributions to the subjects in which he was particularly interested. His many friends will extend their sincere sympathy to his wife, son, and daughters.

E. B. E.

JAMES EDMUND EARL JENKIN, O.B.E.

1893–1957

In the sad death of James Edmund Earl Jenkin on 14 August 1957, after a short illness, the oil industry has lost a wise counsellor, a lovable character, and a firm friend.

He was born in 1893, and his youth was spent in the Lake District, for which part of the country he ever maintained a firm attachment, and to which may be attributed the quality of contentment he derived from the grandeur of nature and the peace of lake and fell. The mountains to be climbed satisfied that side of his nature in overcoming difficulties and achieving the seemingly impossible.

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B B

There is no doubt that it also made him the most modest of men—truly one of nature's gentlemen. He had a passion for outdoor sport in all forms; in later years his main interest was in golf.

His early mechanical engineering training as a premium apprentice in the Barrow works of Vickers Ltd ensured an enduring interest in men. Leaving the diesel engine works, he joined a partnership in Newcastle, which he relinquished in 1920 to join The British Mexican Petroleum Co. He took an active part in the construction and operation of several bunkering terminals, notably those at Southampton, Belfast, and Glasgow.

He became a member of the Institute of Petroleum in 1924, being later elected a Fellow, and a Member of the Institution of Mechanical Engineers in 1937.

In 1925 he surveyed and commenced construction of the terminal at Aruba for Lago Oil, later to become one of the largest refineries in the world. In 1926 he returned to London, becoming assistant chief engineer to the Brit-Mex, Agwi, and Redline group, which later absorbed Glico and became part of the Anglo-American Oil Co.

In 1932 he transferred to the latter when the slump years enforced considerable reorganization in the industry.

The years that followed up to the war were spent in reconstruction in the U.K.

During the war he guided certain Government constructions, for which he was duly honoured with the O.B.E., but which he credited to the efforts of his staff.

In the post-war years he made many journeys abroad for Esso interests, and in 1948 was given the task of organizing the construction of the modern Fawley, where his very pleasant personality helped to build such a fine British/U.S. team which enabled the project to be completed ahead of schedule. At the last he was engaged on future refineries being planned for the U.K. and Eire.

Many of the young men he trained who remain in the industry will ever cherish the memory of a man without enemies but countless friends in all walks of life.

" He never sold the truth to serve the hour,
Nor paltered with the Eternal God for Power."

G. A. V.

RALPH LIONEL SARJEANT

1889–1957

We regret to announce the death of R. L. Sarjeant, a Fellow of the Institute of Petroleum since 1949. He was also a member of the Engineering Committee and as Chairman of the Marketing Sub-Committee played a most important part in drafting the IP Marketing Safety Code, a publication which has been recognized worldwide as a model for safe practice in the petroleum industry.

Mr Sarjeant was, at the time of his death, also Chairman of the Aviation Facilities Sub-Committee which is drawing up an " Airfield Supplement of the IP Marketing Safety Code."

Mr Sarjeant joined The Asiatic Petroleum Company Ltd—now The Shell Petroleum Company Ltd—in 1920, retiring in 1949, and he will be particularly remembered for the work he did during the war on the design of the U.K. pipeline system.

Apart from being a well-trained engineer, he had a most likeable character and will be greatly missed by all his friends and colleagues.

We extend to his widow and children our most sincere sympathy.

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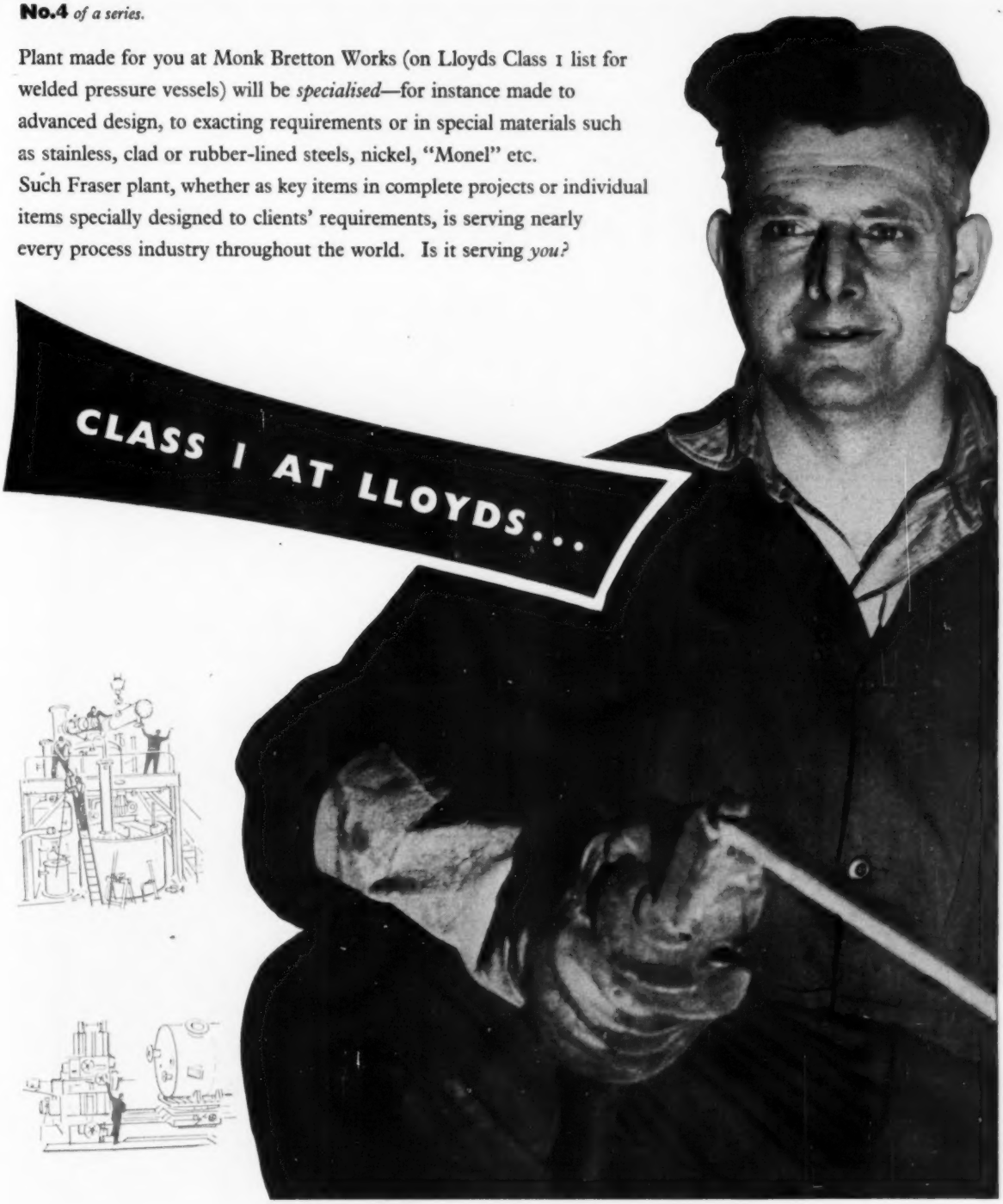

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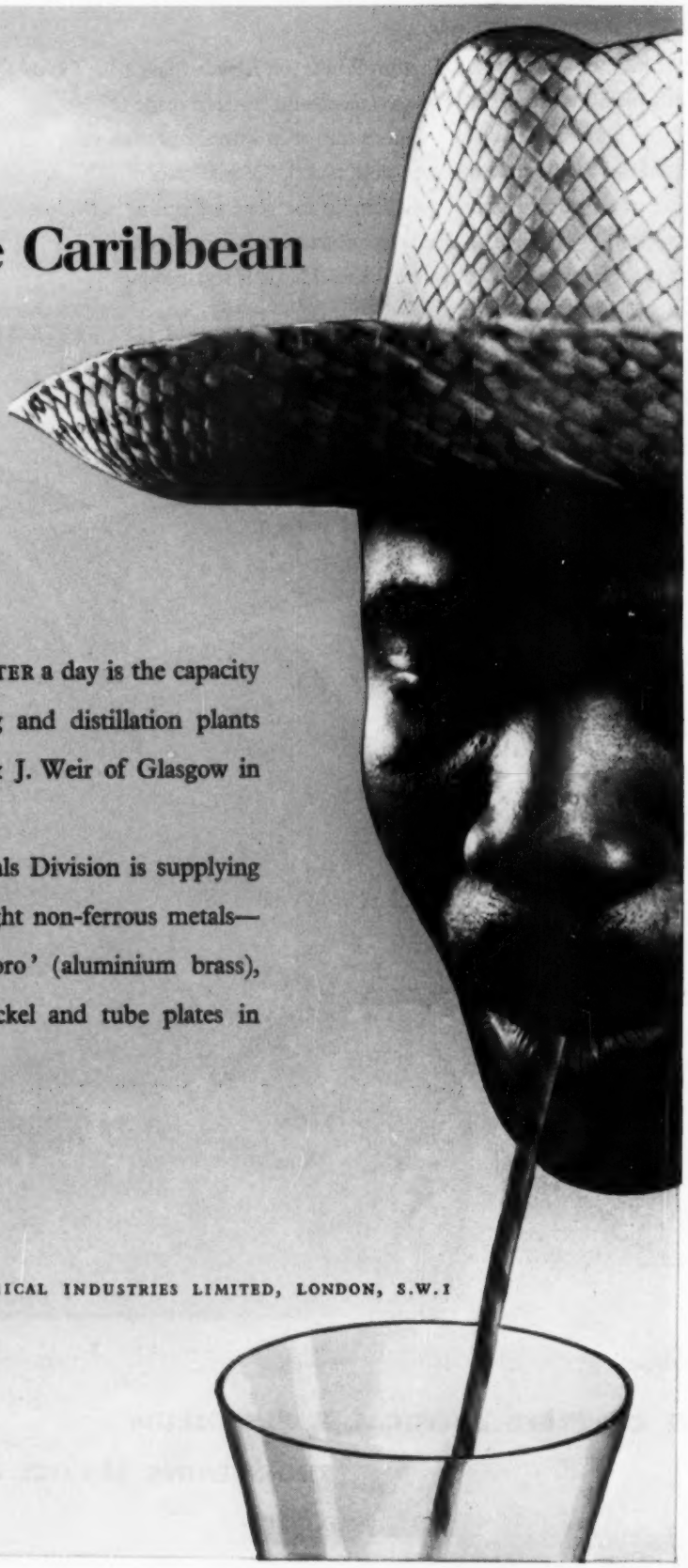

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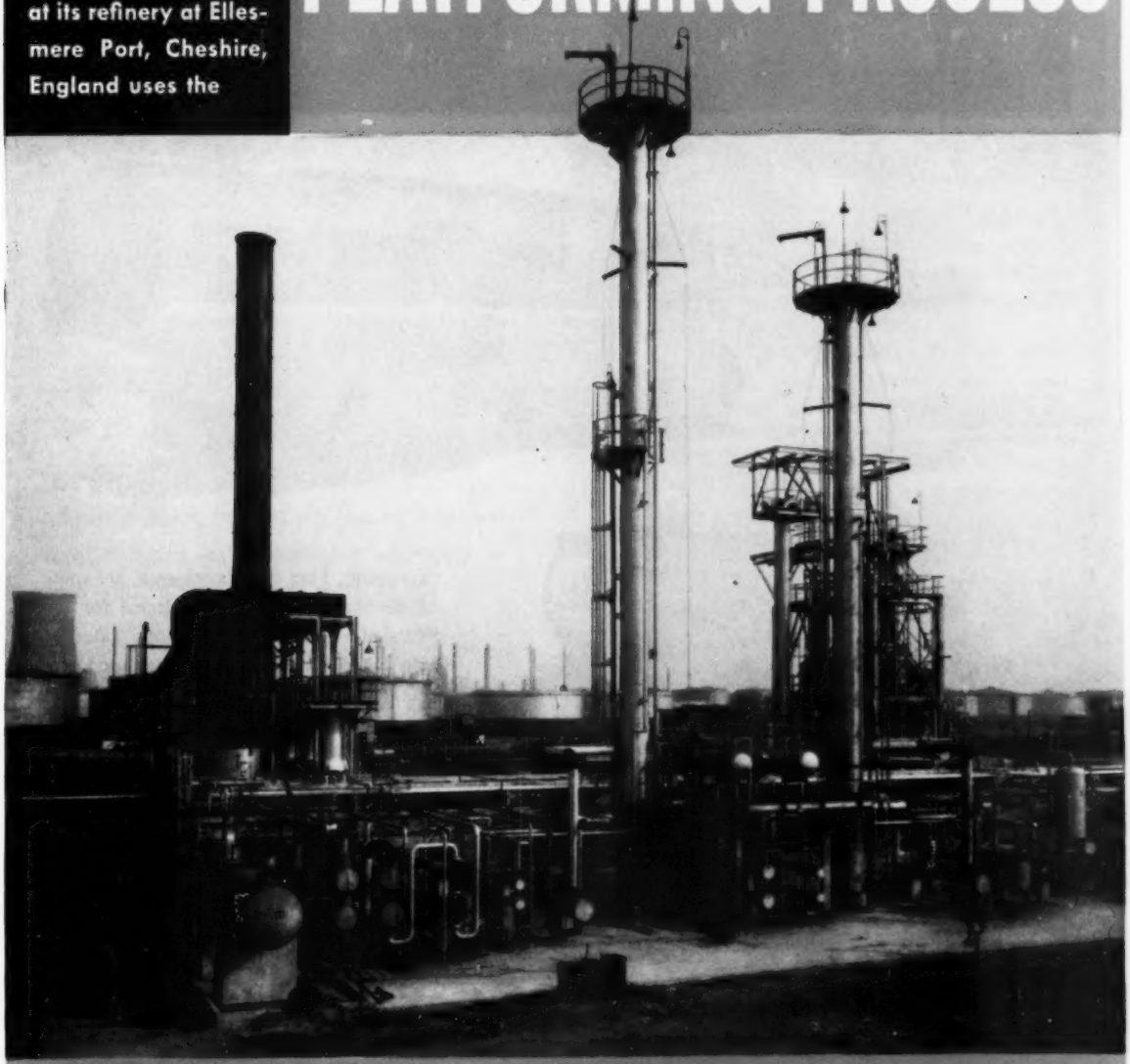

This 800 B/SD Platformer has gone on stream for Lobitos Oilfields, Ltd. producing an 85 to 90 RON clear product from Kuwait naphtha and a 90 to 95 clear blending component from mixed Peruvian naphthas.

Universal Oil Products Company welcomes Lobitos to the large family of refiners throughout the world who use the Platforming Process.

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what ? where ? & how ?

ILLUSTRATED

(Right) A 3,920-gallon 3-compartment Mild Steel Oil Tank mounted on A.E.C. Mammoth Major chassis.

(Below) A 1,500-gallon Mild Steel 3-compartment Light Fuel Oil Tank mounted on Bedford chassis.

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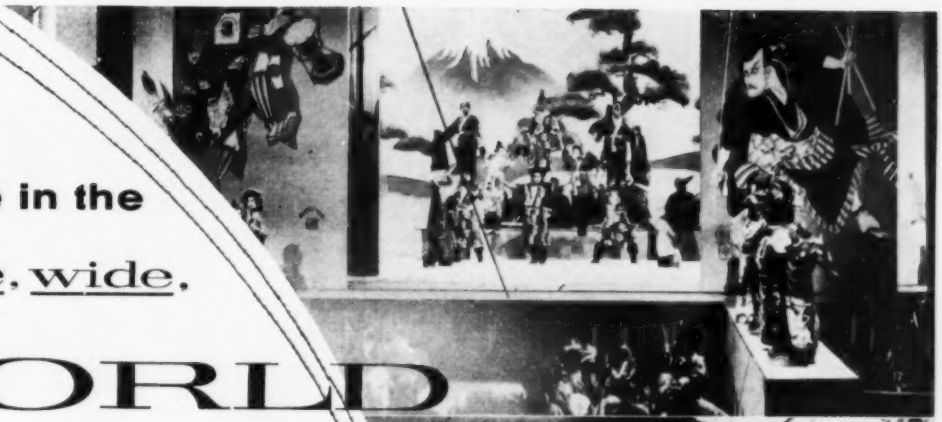
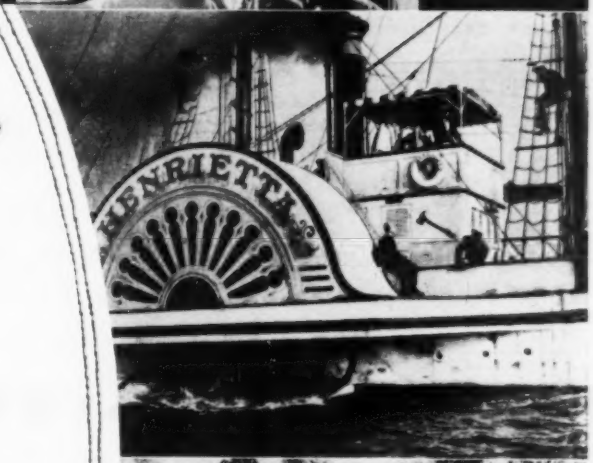


where in the

wide, wide,

WORLD



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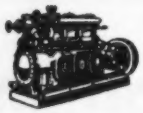

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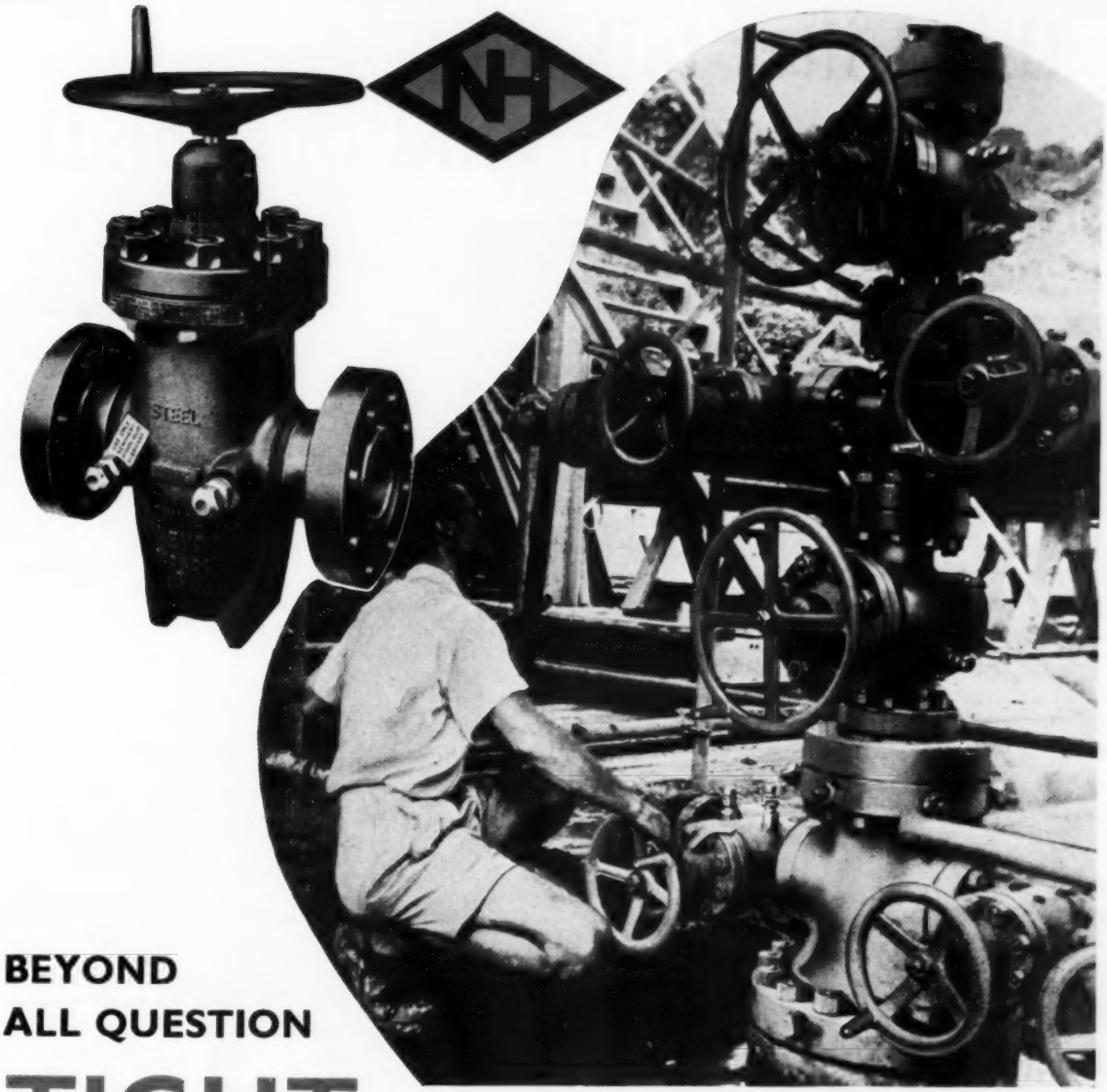

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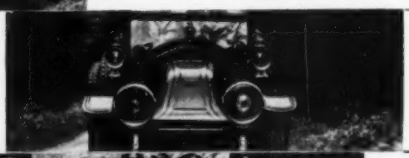
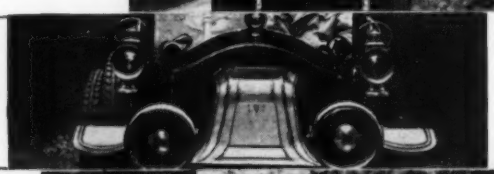
this Filter talk will drive me round the bend!

Sorry, old fruit. I was only trying to be helpful.

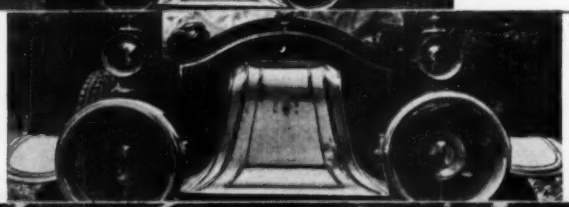
Helpful! Here am I practising for the only real sporting event of the year and all you can talk about is some wretched little gadget on one of your blasted hairyplanes. Can't you see I need to concentrate?



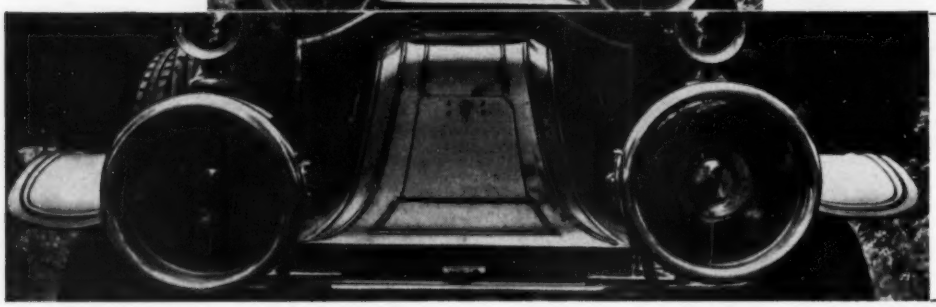
It's not a little gadget and they'd never put it on a plane—it's bigger than this Renault. They put it in the line between the storage and aircraft tanks to make sure the plane gets clean, water-free fuel.



That's the trouble with your infantile modern engines—they have to be fed on strained foods or they get indigestion. Now look at Dotty . . .



Exactly. Do you really think she enjoys having that steam pouring through her exhaust? Now if you took a Simmonds Fram Separator Filter in tow you could have 100% water separation and complete filtration of solids down to 5 microns.



It's tempting, very tempting . . . but it wouldn't be fair on the other competitors. Now d'you mind if we stop a minute . . . I think I really will have to get the rest of that bird's nest out of the tank.

the point of the argument... **FRAM SEPARATOR FILTERS** for clean water-free fuel

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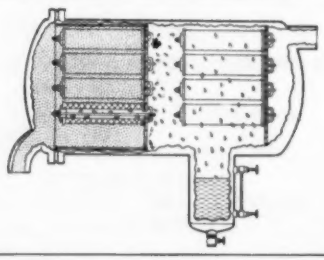

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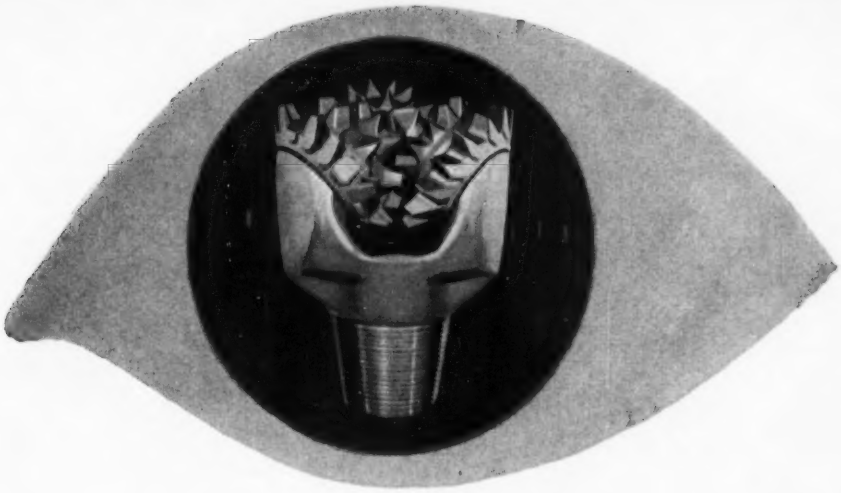
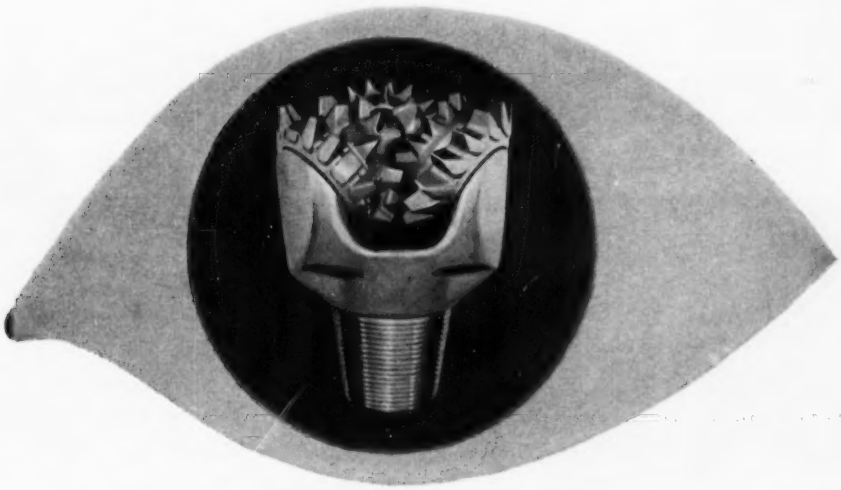


THEY LOOK ALIKE but ...



Looks can be deceiving. Because bits look alike is no assurance they will perform alike.

Just as an example, take the two bits pictured here. What you don't see in the second bit is the increased bearing capacity and other changes that made it a more versatile, longer-lasting, better-performing bit that makes more hole.

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